



Mercury adsorption in the Mississippi River deltaic plain freshwater marsh soil of Louisiana Gulf coastal wetlands

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HIGHLIGHTS

- Freshwater marsh soil has high affinity for mercury.
- Adsorption was controlled by external surface adsorption and intraparticle diffusion.
- Mercury was primarily adsorbed into exchangeable and organic matter sites.
- Adsorption positively affected by phosphate, sulfate or nitrate presence.
- Adsorption negatively influenced by chloride salt and humic acid.

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ABSTRACT

Mercury adsorption characteristics of Mississippi River deltaic plain (MRDP) freshwater marsh soil in the Louisiana Gulf coast were evaluated under various conditions. Mercury adsorption was well described by pseudo-second order and Langmuir isotherm models with maximum adsorption capacity of 39.8 mg g^{-1} . Additional fitting of intraparticle model showed that mercury in the MRDP freshwater marsh soil was controlled by both external surface adsorption and intraparticle diffusion. The partition of adsorbed mercury (mg g^{-1}) revealed that mercury was primarily adsorbed into organic-bond fraction (12.09) and soluble/exchangeable fraction (10.85), which accounted for 63.5% of the total adsorption, followed by manganese oxide-bound (7.50), easily mobilizable carbonate-bound (4.53), amorphous iron oxide-bound (0.55), crystalline Fe oxide-bound (0.41), and residual fraction (0.16). Mercury adsorption capacity was generally elevated along with increasing solution pH even though dominant species of mercury were non-ionic HgCl_2 , HgClOH and Hg(OH)_2 at between pH 3 and 9. In addition, increasing background NaCl concentration and the presence of humic acid decreased mercury adsorption, whereas the presence of phosphate, sulfate and nitrate enhanced mercury adsorption. Mercury adsorption in the MRDP freshwater marsh soil was reduced by the presence of Pb, Cu, Cd and Zn with Pb showing the greatest competitive adsorption. Overall the adsorption capacity of mercury in the MRDP freshwater marsh soil was found to be significantly influenced by potential environmental changes, and such factors should be considered in order to manage the risks associated with mercury in this MRDP wetland for responding to future climate change scenarios.

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1. Introduction

Coastal wetlands between the oceans and land have the ability

to improve coastal water quality and serve as natural habitats for a variety of organisms, as well as inhibiting erosion in the coasts (Wigand et al., 2017). Typically, wetland types in coastal watersheds are classified as salt marshes, freshwater marshes, bottom-land hardwood swamps, and mangrove swamps. These differ depending mainly on their location and salinity. These two factors

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have a significantly impact on the range and scope of plant and animal that can survive and reproduce in these environments (Mitsch and Hernandez, 2013). Especially, freshwater marshes are wetlands containing freshwater water where is usually found near rivers and in low drainage areas. Therefore, the concentration of pollutants in freshwater marsh throughout the year is stable (Swarzenski et al., 2008).

Climate change is a global problem which presents increasing uncertainty in relation to its impacts and consequences (Arnell and Gosling, 2016). Global warming is becoming a major cause of ecosystem destruction and the harsh realities of fatal threats are becoming clearer (Huang et al., 2016). Many researchers are working to mitigate the worst effects of climate change through research on greenhouse gas emissions reduction, renewable energy, environmental monitoring, and pollutant reduction and recycling technologies (Huisinigh et al., 2015; Zhang et al., 2016).

However, sustained levels of sea-level rise and enhanced incidence and duration of storm systems due to climate change will increase the frequency of coastal flooding and inundation, and damage sensitive wetland and estuarine ecosystem services. As sea level rises, their potential self-purification capacities for pollutants as well as ecological (aquatic plants, microbes, and sediments) impacts of wetlands can change due to salt water infiltration in freshwater marsh (Craft, 2012; Clavo-Cubero et al., 2016). At the same time, increase in rainfall due to climate change could cause point and non-point source pollutants from sources such as mine, manufacturing facility, livestock farm, crop field, road and as well as river flooding with contaminants to enter the wetlands (Dai et al., 2016; Haukos et al., 2016; Gill et al., 2017).

Among these pollutants, mercury is the only metal present in liquid form at room temperature, and for centuries it has been one of the most widely used materials from everyday items such as thermometers, batteries, to pesticides, catalysts and caustic soda manufacturing industries (Horowitz et al., 2014; Beckers and Rinklebe, 2017). Mercury and mercury compounds are categorized as representative hazardous substances throughout the world and legal regulations on them are being strengthened (European Parliament, 2008, 2013). Furthermore, mercury in aqueous solution is accumulated in the body due to the uptake of aquatic plants and animals, and adversely affected human health include neurological damage, paralysis, blindness, and chromosomal damage by food chain reactions (US EPA, 1997; National Academy of Sciences, 2000). In particular, mercury in aqueous solutions has been reported to undergo many changes in species differentiation due to dissolution, precipitation, and complexation phenomena under environmental change, which are affected by its adsorption behavior (Bollen et al., 2008; Beckers and Rinklebe, 2017).

However, most studies have only investigated the concentration and distribution characteristics of mercury accumulated in long-term freshwater marsh soil (Kongchum et al., 2006; Sizmur et al., 2016; DeLaune et al., 2016), but their potential adsorption capacity for mercury under various water environmental changes has never been reported. In particular, it is very important to evaluate the potential adsorption capacity of the freshwater marsh soil in order to predict, mitigate and manage the impact of future environmental changes due to climate change on the mercury adsorption capacity of the freshwater marsh soil.

The Mississippi River deltaic plain (MRDP) coastal wetlands are the largest wetlands in the United States, with an area of 11,000 km² from the east of Vermillion bay to the west of the Chandeleur Islands on the southern coast of Louisiana. These coastal wetlands have been subjected to significant loss at a rate of 26–30 km² yr⁻¹ due to subsidence, the lack of sediment inputs as a result of levee system along the Mississippi River as well as the rise of sea level caused by climate change (Wang et al., 2015). The

salinity increase in the coastal wetlands due to sea level rise has been reported to cause ecosystem changes as well as changes in their physicochemical properties (Kassakian et al., 2017). For this reason, it is essential to evaluate the behavior of pollutants in varying environmental conditions for the climate change response of the Gulf coastal wetland freshwater marshes.

Therefore, this study was taken in order to evaluate the potential mercury adsorption characteristics of the MRDP freshwater marsh soil for future environmental changes with emphasis of understanding on (1) the maximum adsorption capacity and adsorption distribution and (2) the adsorption efficiencies of mercury in the MRDP freshwater marsh soils under various conditions.

2. Material and method

2.1. Sample site and properties of freshwater marsh soil

The MRDP coastal wetland freshwater marsh soil used in this study was collected from 0 to 50 cm of the Barataria basin (29°40'N lat. and 90°18'W long.) in Louisiana, USA. The soil in the sample site is classified as Allemands muck (clayey, montmorillonitic, euic, thermic Terric Medisaprist), and the plants are dominated by *Sagittaria lancifolia* and *Panicum hemitomon*. Samples were collected using a McCauly peat auger, transported to laboratory in a cooler, and stored at 4 ± 2 °C before analysis. The analytical method of freshwater marsh soil was described in the supplementary materials, and its characteristics are also shown in S1.

2.2. Adsorption characteristics

2.2.1. Kinetic

Adsorption experiments of mercury by the MRDP freshwater marsh soil were carried out with batch equilibration method. Briefly, stock Hg solutions of 1000 mg L⁻¹ was prepared by dissolving Hg(Cl₂)₂ in DI water. Kinetic experiment on Hg adsorption of the MRDP freshwater marsh soil were performed by weighing 0.05 g of freshwater marsh soil in a centrifuge tubes and adding 25 mL of solution with 200 mg L⁻¹ Hg adjusted to pH 6 by 0.1 M HCl and NaOH. The samples were equilibrated at different time intervals up to 24 h at 25 °C, and separated by centrifugation at 10,000 rpm for 10 min and the supernatant solution was filtered by filter paper (0.45 μm). The concentrations of Hg in residual solutions were analyzed by cold vapor atomic absorption spectrometry according to EPA Method using a Mercury Instruments Analytical Technologies Lab Analyzer Model 254 (Karlsfeld, Germany). The amount of Hg adsorbed per mass unit of the freshwater marsh soil was calculated by difference between initial and equilibrium concentration in solution. Experimental data were described by pseudo-first order (PFO) and pseudo-second order (PSO) models to elucidate the mechanism on mercury adsorption of the freshwater marsh soil (Lagergren, 1898; Ho and McKay, 1998). They are in the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_t and q_e (mg g⁻¹) are adsorbed mercury amount at reaction time t (h) and equilibrium, k_1 (h⁻¹) and k_2 (g (mg·h)⁻¹) are the rate constants for the kinetic models, respectively. The linear plots of $\log(q_e - q_t)$ vs. t for PFO and t/q_t vs. t for PSO can provide adsorption rate constants (k_1 and k_2) from the slope and q_e can be calculated from the intercept, respectively. The intraparticle diffusion model (IPD,

Eq. (3)) was also applied to confirm whether the transport of mercury from the solution to the pores of the freshwater marsh soil is a rate-controlling step (Weber and Morris, 1962).

$$qt = k_i t^{1/2} + C \quad (3)$$

where k_i is the IPD rate constant ($\text{mg g}^{-1} \text{h}^{-1/2}$), C is the intercept.

2.2.2. Adsorption isotherm

Maximum adsorption capacities of mercury by the MRDP freshwater marsh soil in aqueous solution were carried out by Freundlich and Langmuir isotherm models. Briefly, a series of 25 mL mercury suspensions containing different initial concentration ranged from 2.5 to 320 mg L^{-1} in 50 mL centrifuge tubes were prepared, each containing 0.05 g of the freshwater marsh soil. The procedure and analysis of the sample were carried out in the same manner as the above-mentioned kinetic experiments. Adsorption isotherm models were used to fit metal adsorption data for the freshwater marsh soil. The Freundlich (Eq. (4)) and Langmuir (Eq. (5)) equations are expressed, respectively, by

$$q = KCe^{1/n} \quad (4)$$

$$q = \frac{abC_e}{1 + bC_e} \quad (5)$$

where q (mg g^{-1}) is the amount of the mercury adsorbed per unit weight of the freshwater marsh soil, C_e (mg L^{-1}) is the equilibrium mercury concentration in solution. K and a (mg g^{-1}) are the constants representing mercury adsorption capacity of Freundlich and Langmuir isotherm models, respectively. The adsorption intensity ($1/n$) and binding strength (b) were calculated from Freundlich and Langmuir isotherm models, respectively.

2.2.3. Mercury fraction

Fractionation experiments of mercury-adsorbed marsh soil were performed by the sequential extraction method reported by Zeien and Brümmer (1991). Briefly, 0.05 g of mercury-adsorbed freshwater marsh soil was mixed with extract solution of 10 mL in centrifuge tubes and the mixture was shaken at 160 rpm (25 °C) according to each metal extraction process. The samples were centrifuged at 10,000 rpm for 10 min followed by filtration of supernatant using 0.45 μm membrane filter. The soil residue remaining after each extraction reaction was washed with DI water and dried until the remaining solution was completely evaporated according to a procedure described by Rinklebe and Shaheen (2014). The extraction solutions and their detail conditions used in this experiment are summarized in Table S2 (See Supplementary Materials) (Rinklebe and Shaheen, 2014). The sum of mercury extracted from sequential extraction ($\Sigma\text{F1–F7}$; where the fraction of F1, F2, F3, F4, F5, F6 and F7 indicates mercury forms of soluble + exchangeable, easy mobilizable, manganese oxide-bound, organic, amorphous iron oxide-bound, crystalline iron oxide-bound, and residue, respectively) was compared with the results obtained by adsorption experiment and the recovery was calculated as follows:

$$\text{Recovery (\%)} = 100 \times [(\Sigma\text{F1–F7})/\text{amount of mercury adsorbed}] \quad (6)$$

2.2.4. Effects of various factors on mercury adsorption

Mercury adsorption characteristics of the MRDP freshwater marsh soil in aqueous solution reaction were evaluated through various conditions including initial pH (2–10), temperature

(25–45 °C), background electrolyte concentration (0.01–0.50 M NaCl), other ligands (SO_4^{2-} , PO_4^{3-} , NO_3^- , and humic acid) and competitive metals (Cu, Pb, Cd, and Zn). Basically, the experiments were performed by weighing 0.05 g of the soil sample in centrifuge tubes of 50 mL followed by additions of 25 mL of solution with 200 mg L^{-1} mercury. The experiment of mercury adsorption capacity of the marsh soil was carried out in mercury solution as HgCl_2 of 200 mg L^{-1} containing either 0.01 M SO_4^{2-} , PO_4^{3-} , NO_3^- as potassium salts, humic acid or 200 mg L^{-1} competitive metals as chloride salts at pH 6. The procedure and analysis of the sample were carried out in the same manner as the above-mentioned kinetic experiments.

3. Results and discussions

3.1. Adsorption kinetic

The effect of reaction time on mercury adsorption of the MRDP freshwater marsh soil for evaluating adsorption kinetic is shown in Fig. S1. The mercury adsorption was rapid in the first 4 h and then slowly reached equilibrium after 24 h. The fact that the fast initial rate of adsorption during the first 4 h of contact was followed by a slower one until equilibrium state suggests that there are various active sites that are likely to adsorb mercury on the freshwater marsh soil surfaces. The adsorption rate is significantly reduced as the mercury is increasingly saturated with the active sites of the freshwater marsh soil. These results were consistent with the findings of other authors that used clay and sediments (Manohar et al., 2002; Hintelmann and Harris, 2004). To understand adsorption mechanism, the PFO and PSO models were used to investigate adsorption kinetics of mercury onto freshwater marsh soil (Fig. S1). The values k_1 and k_2 , calculated q_e values determined from the PFO and PSO model along with the corresponding correlation coefficients (R^2) are presented in Table 1. These results indicated that the PSO ($R^2 > 0.9961$) fit the data better than the PFO ($R^2 = 0.9092$), suggesting that the PSO can be applied for the entire adsorption process. These results indicate that the reaction rate is proportional to the number of the active sites present, confirming that chemisorption was the rate-limiting for the adsorption of mercury. In addition, the IPD model, which explains adsorption process that may involve several different steps (Wu et al., 2009; Arias et al., 2017), was used to provide a partial description of the adsorption rate of mercury in the freshwater marsh soil. It is confirmed that the shape of the IPD model fit of experimental data is well separated into two straight lines at the contact time 4 h (please see supplementary material Fig. S1D). The first straight line is adsorption due to the external surface adsorption during which the mercury moves from the bulk of the solution to the marsh soil surface, while the second straight line is adsorption due to pore diffusion (Table 1). At the beginning of the reaction time, mercury was adsorbed rapidly on the marsh soil surface by the dispersion of the boundary layer, and after 4 h, the adsorption reaction occurred slowly through the pore diffusion. Further, the mercury adsorption kinetic of the freshwater marsh soil was dominated by the external surface adsorption (external mass transfer), and the adsorption reaction into pores (intraparticle diffusion) is an additional factor. These results suggest that the adsorption mechanism of mercury in the MRDP freshwater marsh soil was complex and affected by both the external mass transfer to the surface and the intraparticle diffusion. Similar phenomenon was also reported in the mercury adsorption by vermiculite (do Nascimento et al., 2016).

3.2. Adsorption isotherm

The adsorption capacity of mercury by the MRDP freshwater

Table 1

Parameters for mercury adsorption kinetics and isotherms of freshwater marsh soil.

Kinetics		
Pseudo first order	q_e (mg g ⁻¹)	26.5
	k_1 (h ⁻¹)	0.157
	R^2	0.908
Pseudo second order	q_e (mg g ⁻¹)	38.0
	k_2 (g mg ⁻¹ h ⁻¹)	0.009
	R^2	0.996
Intraparticle diffusion	k_i (mg g ⁻¹ h ^{-1/2})	2.798
	C (mg g ⁻¹)	20.4
	R^2	0.985
Isotherms		
Freundlich	K	2.635
	$1/n$	0.585
	R^2	0.880
Langmuir	a (mg g ⁻¹)	39.8
	b (L mg ⁻¹)	0.066
	R^2	0.997

marsh soil was evaluated by adsorption isotherm and the adsorption isotherm data were fitted with Freundlich and Langmuir models (Fig. S2 and Table 1). Freundlich isotherm calculated adsorption coefficient (K) for mercury was 2.635 with $1/n$ values were less than unity, representing a favorable adsorption process. On the other hand, the maximum adsorption capacities (a) of mercury determined based on the Langmuir model was 39.8 mg g⁻¹. Experimental data of mercury adsorption was generally better described by Langmuir model ($R^2 = 0.997$) than Freundlich model ($R^2 = 0.880$). While the Freundlich model considers heterogeneous surfaces with molecules adsorbed to surface activate site of adsorbents, the Langmuir model considers adsorption by a monolayer onto a homogenous surface with constant adsorption energy (Volesky, 1994; Eloussaief et al., 2013; Shaheen et al., 2013). Therefore, the adsorption of mercury was primarily affected by the monolayer onto homogeneous surface of freshwater marsh soil.

Table S3 (See Supplementary Materials) presents the comparison of the MRDP freshwater marsh soil with other soils and clay mineral adsorbents such as montmorillonite, bentonite and vermiculite for mercury adsorption reported in literature. While it may be difficult to make direct comparison due to the physico-chemical properties of these soils and the conditions used in experiments, it is, nonetheless, clear that the maximum adsorption capacity of 39.8 mg g⁻¹ of this MRDP freshwater marsh soil is much higher than 0.2–12.7 mg g⁻¹ for many soils. The significantly high OM (23.0%) or TOC (398 g kg⁻¹) of the MRDP freshwater marsh soil was likely responsible for the observed high mercury adsorption capacity over those soils which contained 0.53–1.65% OM or 15.7–19.5 g kg⁻¹ TOC (Yang et al., 2008; Ding et al., 2017) since organic matter was known to have higher affinity for mercury (Kabala and Singh, 2001; Jiang et al., 2015). In addition, the adsorption capacity of the MRDP freshwater marsh soil is also much higher than those of natural clays and clay minerals used as adsorbents such as bentonite, montmorillonite, vermiculite, and zeolite, but similar or lower than those adsorbents of clay minerals and diatomite modified with functional group impregnation of aluminum, nitrogen, sulfur and halide for enhancement of mercury adsorption capacity (Wang et al., 2011; Eloussaief et al., 2013; Caner et al., 2015). These comparisons emphasize the strong mercury adsorption capacity of the freshwater marsh soil.

3.3. Fractionation of mercury

Fig. 1 shows the partition of adsorbed mercury by the MRDP freshwater marsh soil into different binding pools in terms of

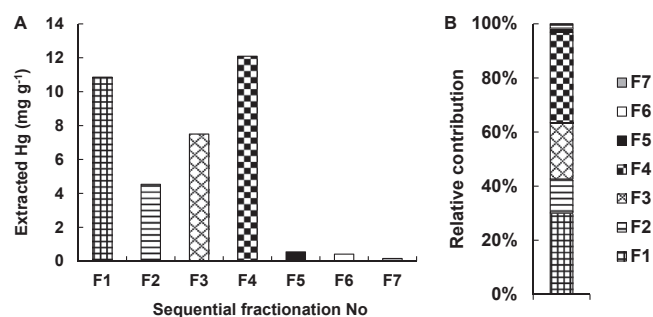


Fig. 1. Amount of Hg extracted from the MRDP freshwater marsh soil at each step (A) and relative contribution (B) of sequential fraction.

absolute amounts (Fig. 1A) and relative percentage (Fig. 1B) by sequential extraction. The recovery of mercury ranged in average between 93.6% and 109.0% indicated general agreement of result by the sequential extraction procedure. Amount of mercury extracted (mg g⁻¹) at each step was in order of F4 (12.09) > F1 (10.85) > F3 (7.50) > F2 (4.53) > F5 (0.55) > F6 (0.41) > F7 (0.16). The amount of mercury extracted from F1 to F4 accounts for about 98.3% of the total extracted mercury (36.10 mg g⁻¹). The mercury was largely adsorbed by soluble and exchangeable (F1) and organic matter (F4) sites in freshwater marsh soil. In general, the adsorption of heavy metal in soils and sediments has been reported to be dominantly influenced by organic matter, exchangeable cations and Fe- and Mn-(hydr)oxides (Kabala and Singh, 2001). Especially, the adsorption of mercury is well known to have a high affinity for organic matter with functional group such as S, N, and O in soil and sediment, and its affinity is reported to be higher than that of soil minerals and metal oxides (Schlüter, 1997; Jiang et al., 2015).

Rinklebe and Shaheen (2014) reported F1–F2 as mobility fraction and F3–F6 as a potential mobility fraction of mercury, indicating that their adsorption forms are relatively weak or moderate bonding strength, which is potentially mobile due to environmental changes such as temperature, pH, and the influx of other contaminants. Especially when considering the heavy metals adsorbed in the soil, it is important to evaluate whether or not these heavy metals are absorbed into plants and threaten human health according to their presence within the food chain (Chen et al., 2016). Mercury is not easily absorbed into plants in a relatively stable state when it is bound to silicates and other primary and secondary minerals in the soil lattice. On the other hand, bioavailable mercury is easily transported and absorbed by plants (Gochfeld, 2003). Li et al. (2009) reported that bioavailable mercury includes soluble and exchangeable fraction (F1) along with carbonate bond fraction (F2). In our study, bioavailable mercury accounted for 42.6% of the total extracted mercury with the F1 and F2 accounted for 30.1% and 12.6%, respectively (Fig. 1B). These results suggested that even though the potential for mercury adsorption in the MRDP freshwater marsh soil is high, there is still a potential risk of mercury threat to organisms because the bioavailable adsorption form is also high.

3.4. Effect of pH

Solution pH is a main factor in an adsorption system involving multifunctional charged macro molecules and metal ions, as pH can affect the dissociation of cation exchange groups, conformational changes of molecular structure, stability of metal complexes and speciation of metals (Jiskra et al., 2014). Fig. 2A illustrates the influence of pH on mercury adsorption by the MRDP freshwater marsh soil. As solution pH increased from 2 to 10, the amount of

mercury adsorbed by the freshwater marsh soil increased from 9.8 to 51.5 mg g⁻¹ in a near linear fashion. The results in this study are in agreement with that of Semu et al. (1987) for tropic Tanzania soils, but different from that of Yin et al. (1996) who found a general decreased Hg(II) adsorption in fifteen New Jersey soils as pH increased from 4 to 9. Yin et al. (1996) attributed the decreased Hg adsorption to the significant release (desorption) of dissolved organic matter as soil pH increased as well as much low Hg concentration [Hg(II) at 10⁻⁷ M] used in their study as compared to that of Barrow and Cox (1992) who found that such a decrease was much less at Hg(II) concentrations > 10⁻⁴ M. On the other hand, the MRDP freshwater marsh soil contains 39.8% carbon (Table S1) and only a very small fraction of dissolved organic carbon (DOC) in such soil (Dodla et al., 2012). The release of DOC-complexed Hg as pH increased may be much smaller than the larger portion of increased Hg(II) adsorption due to Hg complexation with insoluble organic matter. In addition, how Hg(II) adsorptive was introduced into the suspensions of adsorbents (soils or minerals) appeared to make significant difference relative to the pH effect on Hg(II) adsorption. In the study of Semu et al. (1987), Hg(II) was added to soil as HgCl₂ (similar to our study) which resulted in the increased Hg(II) adsorption as pH increased with the maximum adsorption at pH 8–9. On the other hand, when Hg(II) was introduced as Hg(NO₃)₂, Hg(II) adsorption maximized at pH 3.5–5.0 and a further pH

increase generally decreased Hg(II) adsorption (Barrow and Cox, 1992; Yin et al., 1996). Sarker et al. (1999) later demonstrated this difference of Hg(II) adsorption in quartz and gibbsite systems under chloride, nitrate and other salt background and concluded that the occurrence of Hg(II) adsorption edge (maximum) as a result of pH change depended on the specific pH that promoted the formation of aqueous Hg(OH)₂ in the presence of each electrolyte system. The aqueous Hg(OH)₂ has been suggested as the major form of mercury adsorption by various soil constituents (Semu et al., 1987; Bäckström et al., 2003; Frohne and Rinklebe, 2013; Jiskra et al., 2014; Zhang et al., 2014) and the presence of chloride inhibits its formation (Farrah and Pickering, 1977; Barrow and Cox, 1992; Sarker et al., 1999). In our study, the main species of mercury between pH 3 and 10 are HgCl⁺, HgCl₂, HgClOH and Hg(OH)₂, but the Hg(OH)₂ became dominated at about pH 7 and 100% at about pH 8.5 (Fig. S3), corresponding to the maximum adsorption of mercury (Fig. 2A). In addition, besides the promotion of Hg(OH)₂ formation, increasing pH is known to disperse humic substances (Sparks, 2003), which likely enhances the exposure of reactive sites for mercury species. High pH increases Hg(II) complexation with carboxyl functional groups of organic matter (Dong et al., 2013; Jiang et al., 2015). Therefore, the pH of the influent flowing into the MRDP freshwater marsh soil is considered to be an important factor affecting the adsorption capacity of mercury.

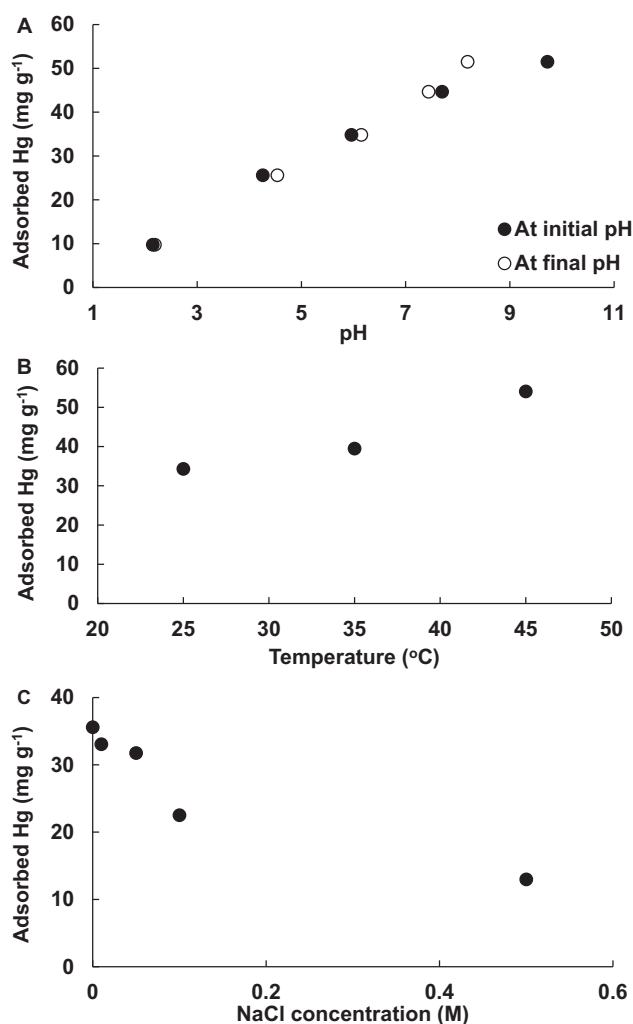


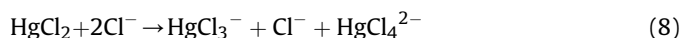
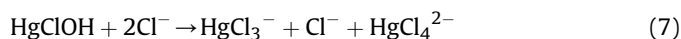
Fig. 2. Effect of pH (A), temperature (B), and NaCl concentration (C) on mercury adsorption by the MRDP freshwater marsh soil.

3.5. Effect of temperature

Temperature effect on mercury adsorption by the MRDP freshwater marsh soil was conducted at pH 6. The amount of mercury adsorbed by the freshwater marsh soil at 25, 35, and 45 °C were 34.3, 39.5, and 54.1 mg g⁻¹, respectively (Fig. 2B). The result indicates that the adsorption of mercury to freshwater marsh soil is highly preferred at high temperature, suggesting that the adsorption process is endothermic in nature. On the other hand, because diffusion is known as an endothermic process (Krishnan and Anirudhan, 2002), this would suggest that the adsorption capacity of mercury would be improved by diffusion facilitation through increasing the environmental temperature. The same phenomenon also has been observed in clay soil by Manohar et al. (2002).

3.6. Effect of ion strength

In this study, mercury adsorption characteristics of the MRDP freshwater marsh soil were compared by varying background solution ionic concentration of NaCl. The amounts of mercury adsorbed by the freshwater marsh soil generally decreased as NaCl concentration increased from 0 (control) to 0.50 M (or from 35.6 to 13.0 mg g⁻¹) with significant effect at high NaCl concentration > 0.10 M (Fig. 2C). This was likely caused by increasing Cl⁻ effect on the formation of ionic HgCl₄²⁻ from non-ionic HgClOH or HgCl₂ complexes as (Zhang et al., 2010):



In general, HgClOH and HgCl₂ are predominant in low chloride ion concentrations, while HgCl₄²⁻ is predominant in high chloride ion concentrations (Kim and Lee, 2014). Thus, the increase in Cl⁻ concentration dominated competition with OH⁻ by forming the Hg–Cl complexes, and these complexes substantially decreased mercury adsorption capacity due to the low affinity for the freshwater marsh soil because of generally negatively charged soil particles.

3.7. Effects of other pollutants

Nonpoint pollutants are introduced into wetlands through various routes, and especially during heavy rainfall, the amount of pollutants entering roads and agricultural lands increases. In particular, sulfate, phosphate, nitrate, and humic acid and heavy metals are typical water pollutants, and they have been reported to have a great influence on heavy metal adsorption (Jiskra et al., 2014; Jiang et al., 2015). The effect of these ligands and heavy metals on the capacity of mercury adsorption by the MRDP freshwater marsh soil was also investigated.

3.7.1. Sulfate, phosphate, nitrate and humic acid

The effects of coexisting ligands of sulfate, phosphate, nitrate and humic acid on the adsorption of mercury at pH 6 are shown in Fig. 3A. The amounts of mercury adsorbed by the MRDP freshwater marsh soil in the presence of these ligands were 54.7 mg g^{-1} for SO_4^{2-} , 57.6 mg g^{-1} for PO_4^{3-} , 42.9 mg g^{-1} for NO_3^- , and 18.9 mg g^{-1} for humic acid. Comparing to 37.7 mg g^{-1} of mercury adsorbed by the freshwater marsh soil in pure mercury solution (control), the presence of SO_4^{2-} , PO_4^{3-} or NO_3^- improved the mercury adsorption capacity. According to Farrah and Pickering (1977), solution mercury could be reduced by precipitation/adsorption when the concentration of sulfate and phosphate to mercury is above 1:1 M ratio, which was the case in our study with the molar concentrations of sulfate and phosphate about 10 times higher than that of mercury. On the other hand, due to the strong inhibition of chloride on mercury adsorption caused by the formation $\text{Hg(II)}\text{--Cl}$ complexes, which have little or no affinity for soil particle surface (Sakar et al., 1999), it would be expected that generally strong adsorption of mercury by the freshwater marsh soil in the presence of phosphate, sulfate or nitrate at pH 6 in this study. In addition, the fact that phosphate ligand yielded the highest mercury adsorption could be due to strong bridging effect of phosphate between Hg(OH)_2 and soil constituents (Sarker et al., 1999).

On the other hand, the adsorption efficiency of the MRDP freshwater marsh soil in humic acid-containing mercury solution was reduced by 49.9% as compared with that in pure mercury solution (control). Humic acids in aqueous solution generally have a high affinity for metals due to the presence of various functional groups such as carboxyl, hydroxyl, and thiol (Ravichandran, 2004). Especially, the thiol group (R-SH) in humic substances has been shown to form the most stable Hg complexes over a wide range of pH in soil and water (Jiang et al., 2015).

These results have significant implications as the freshwater marsh is influenced by seawater intrusion, which contains both Cl^- and SO_4^{2-} with Cl^- concentration of 5–6 times greater than SO_4^{2-} . It would be likely to see increased mercury release from soil at low pH but decreased at high pH. In addition, the introduction of pollutants such as phosphate and nitrate from stormwater runoff also would increase mercury adsorption in the freshwater marsh soil. While the humic acid present in the soil solution would generally decrease mercury adsorption capacity but its impact could be easily inversed as it bonds to soil particles or becomes precipitated in low soil pH environment.

3.7.2. Heavy metals

The influence of other heavy metals on mercury adsorption in the MRDP freshwater marsh soil was shown in Fig. 3B. These metals were selected for evaluation due to their often co-presence with Hg (Uddin, 2017). In general, these heavy metals significantly reduced Hg from 34.3 mg g^{-1} to 13.9, 9.5, 24.2 and 17.9 mg g^{-1} for Cu, Pb, Zn, and Cd, respectively. Competing effects of heavy metal ions on mercury adsorption were in the order of $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$, and the selectivity of the freshwater marsh soil for Pb and Cu adsorption was better than that of Cd and Zn. The higher the electronegativity of atoms, the greater the adsorption of ionic form by a charged adsorbent surface can be assumed (Park et al., 2016). The electronegativity of the heavy metals used in this experiment was higher in the order of $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$ (McBride, 1994). In the binary metal systems, the adsorption capacity of mercury is suppressed by the presence of other metal ions in aqueous solution. As a result, the influx of other heavy metals into the wetlands could be an important factor in reducing the mercury adsorption capacity of freshwater marsh soil. In addition, since most wastewater contains mixed heavy metals in complexed forms with each one potentially existing more than two species, additional experiments are needed to determine the competitive adsorption characteristics and heavy metal adsorption sequence in the MRDP freshwater marsh soil.

4. Conclusions

This study demonstrated that the mercury adsorption characteristics of the MRDL freshwater marsh soil in Louisiana Gulf coast was significantly influenced by potential change in water environmental conditions. The mercury adsorption by the MRDP freshwater marsh soil was well described by pseudo-second order and Langmuir isotherm models. The kinetic experiment also showed that the mercury adsorption was controlled by both the external surface adsorption and the intraparticle diffusion. Amount of mercury adsorbed (mg g^{-1}) in the freshwater marsh soil was partitioned into different fractions in the order of $\text{F}_4 (12.09) > \text{F}_1 (10.85) > \text{F}_3 (7.50) > \text{F}_2 (4.53) > \text{F}_5 (0.55) > \text{F}_6 (0.41) > \text{F}_7 (0.16)$, with organic matter and soluble/exchangeable fractions accounting for 63.5% of total adsorption. The decrease in mercury adsorption to the freshwater marsh soil was strongly influenced by NaCl concentration increase, competing heavy metals, and the presence of the humic acid, while the increase in temperature and pH generally increased the mercury adsorption capacity. In addition, the presence of phosphate, sulfate and nitrate also enhanced mercury

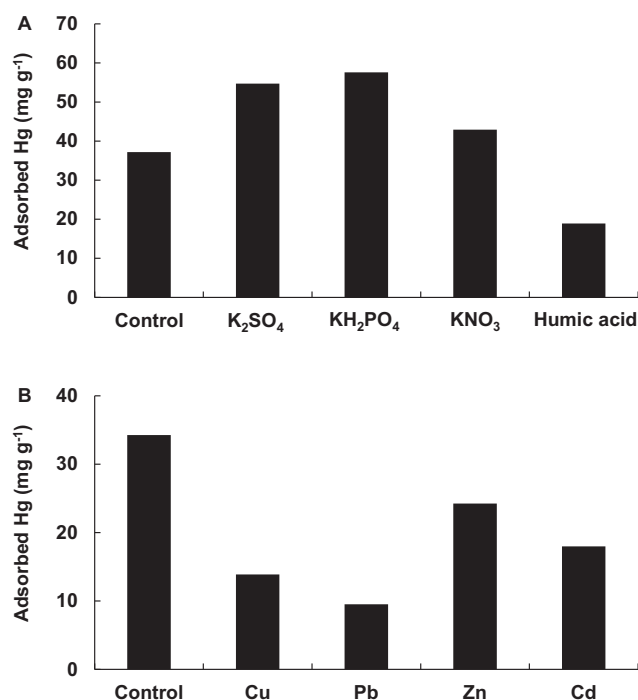


Fig. 3. Effects of coexist ligands (A) and competitive metal ions (B) on mercury adsorption onto the MRDP freshwater marsh soil.

adsorption. As such, attention needs to focus on these factors in order to develop ways to reduce and manage mercury risk in the Gulf coastal wetlands in response to future climate change scenarios.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2017.12.104>.

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